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## Intermediates and Dyestuffs for Synthetic Fibres. Part II.† Halogeno-2-aminobenzothiazoles

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The preparation of 4-, 5-, 6-, and 7-chloro-, -bromo-, and -fluoro-2-aminobenzothiazoles is described. Ultraviolet and infrared absorption spectra of these, and of a series of halogenophenylthioureas, are recorded.

2-AMINOBENZOTHIAZOLES have been widely used as diazo-components in monoazo disperse dyes. Many dyes have been recorded from 6-substituted 2-aminobenzothiazoles, e.g., alkyl,<sup>1</sup> chloro-,<sup>1</sup> and alkylsulphonyl,<sup>2</sup> but with the exception of some 4,6-disubstituted analogues,<sup>3</sup> few data are available on the use of isomeric derivatives. This present work records the synthesis

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- <sup>3</sup> Interchem. Corp., U.S.P. 3,057,848; 1.C.1., B.P. 896,232; Sandoz, B.P. 868,037 <sup>4</sup> R. C. Elderfield and F. W. Short, J. Org. Chem., 1952, 17,
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and spectra of a series of halogenated 2-aminobenzothiazoles.

6-Substituted 2-aminobenzothiazoles have been prepared by thiocyanation and cyclisation of 4-substituted anilines, using bromine and alkali-metal thiocyanate 4-6 or cupric thiocyanate in solvents; 7-9 bromine has has been replaced by sulphuryl chloride,  $^{10}$  NN-dichlorourea,<sup>11</sup> N-chloroacetamide,<sup>12</sup> and NN-dichloropenta-

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methylenetetramine; <sup>13</sup> thiocyanogen for the reaction has also been obtained by electrolysis methods.<sup>14-16</sup>

4- and 6-Substituted 2-aminobenzothiazoles result from cyclisation of 2- and 4-substituted N-arylthioureas with bromine,17 sulphuryl chloride,18,19 chlorine,20 sulphur dichloride,<sup>18,19</sup> or antimony pentachloride<sup>21</sup> in chloroform, chlorobenzene, ethylene dichloride, or nitrobenzene. The arylthioureas, initially obtained from ammonia and aryl isothiocyanates,<sup>22-24</sup> are more conveniently derived from arylamines by reaction with alkali-metal thiocyanate in aqueous or organic media in presence of acid.<sup>25-27</sup> Similar cyclisation of 3-substituted arylthioureas gives mixtures of 5- and 7-substituted 2-aminobenzothiazoles, the ratios depending on the substituent.<sup>28-30</sup> A less ambiguous synthesis, adopted in the present work is outlined in the Scheme.



By variations of the above general methods, 4-, 5-, 6and 7-halogeno-2-aminobenzothiazoles were obtained. Thiocyanation-cyclisation sequences from 4-halogenoanilines afford 6-chloro- and 6-fluoro-2-aminobenzothiazoles in good yield; yields of 6-bromo-2-aminobenzothiazole were low by this method, but were con-

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siderably higher by cyclisation of 4-bromophenylthiourea.

Cyclisation of *o*-fluorophenylthiourea with bromine in chloroform tended to result in preferential formation of a bromo-fluoro-2-aminobenzothiazole, presumably 6-bromo-4-fluoro-, and modified cyclisation conditions were required to produce 4-fluoro-2-aminobenzothiazole.

5- and 7-Halogeno-derivatives were obtained by methods based on the Scheme. Nitration of 2-halogenoacetanilides gave a mixture, separated by preferential solubility of the 6-nitro-isomer in Witt-Utterman solution.<sup>31,32</sup> Diazotisation, for subsequent reaction with cuprous thiocyanate, was best effected in glacial acetic acid or 50% sulphuric acid; reductive cyclisation of the o-nitrothiocyanato-compounds occurred in several media and methods based on hydrogen reduced iron and tin-hydrochloric acid were found to be most useful.

Spectra of Arylthioureas.—Arylthioureas may be compared to the arylureas, the u.v. spectra of several of which have been reported,<sup>33-36</sup> and principal bands for the arylthioureas (Table 1) are bathochromically displaced compared with analogous arylureas. As with arylureas,<sup>37</sup> the wavelength of both absorption bands decreases for substituent orientation  $\phi > m > o$ , but in the present series, band intensities do not follow previously reported orders and are relatable neither to I or M effects alone.

Principal i.r. bands in regions normally associated with NH stretching frequencies are given in Table 2. In compounds RNH·CO·NH<sub>2</sub>, three bands are observed R=alkyl, but only two where  $R=aryl\,^{38}$  and in 1-p-tolylthio-3-alkylureas 39 and the corresponding sulphones. The halogenoarylthioureas show one sharp well defined band in the 3400 cm.<sup>-1</sup> region and other broader bands, and the absence of any significant bands which could be associated with either  $\nu$ (C=NH) or  $\nu$ (C=NH<sup>+</sup>) indicates a predominant contribution of a benzenoid structure (also shown 40 by magnetic susceptibility measurements).

The broad fairly strong bands in the 3170-3190 cm.<sup>-1</sup> region are at a frequency not normally associated with

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U.v. absorption maxima of arylthioureas in absolute ethanol

ethenor						
Subst. in Ph ring	${}^{1}L_{b}{}^{-1}A$	${}^{1}L_{A} - {}^{1}A$				
н	242 sh (4.02)	270(4.24)				
<i>p</i> -OMe	• •	270 (4.13)				
b-Cl	240(4.01)	272(3.99)				
m-Cl	240(4.09)	276(4.18)				
<i>p</i> -Cl	242(4.13)	<b>277</b> (4·18)				
<i>p</i> -Br	· · ·	276 (3.98)				
<i>m</i> -Br	238sh (4·16)	276(4.16)				
<i>þ</i> -Br	245 (4.23)	277 (4·36)				
<i>b</i> -F	236(4.05)	268(4.04)				
<i>m</i> -F	. ,	269(4.17)				
þ-F	238 (4.00)	269(4.09)				
	• •	· ·				

monomeric NH<sub>2</sub>, and it seems likely that some association is present under the conditions in which the spectra were recorded. The 3400 cm.<sup>-1</sup> band is assigned to NH stretching of the imino-group, since this is the NH2 group with hetero N of another molecule) and  $3500 \text{ cm}^{-1}$  (perturbation resulting from association).

TABLE	2
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Subst. in Ph rir	ıg		
н	3421s	3270m, br	3170s,br
<i>p</i> -OMe	3402s	3280m	3165s,br 3120m
o-Cl	3350m,br	3260s,br 3230s	3165sh
<i>m</i> -Cl	3415s	3280s	3168s 3138m
<i>p</i> -Cl	3415s	3270s,br	3188s 3140m
o-Br		3295w	3190s
<i>m</i> -Br	3408s	3270m,br	3185m
			3160s,br
<i>p</i> -Br	3409s	3270s,br	3190vbr,s
o-F	3420s	3260s 3238s	3158s
<i>p</i> -F	<b>3440</b> s	3278m	3175s,br 3130m

Absence of characteristic  $\nu(C=N)$  and  $\nu(C=N^+)$  bands indicates the absence of (II), in agreement with results

TABLE 3

U.v. absorption maxima of halogenated 2-aminobenzothiazoles (in ethanol)

Subst. in Ph ring	r				7	
н	224 (4.55)			277 (4.28)	293sh (3·86)	
4-C1	232 (4·55)		268sh (3.89)	271 (4·08)	· · ·	$300 \text{sh} (3 \cdot 21)$
5-Cl	232(4.59)	257sh (3·03)	264 sh (3.72)	272 (4·00)	<b>296 (3·60)</b>	304 (3.59)
6-Cl	227(4.55)	258 sh (3.54)	264sh (3·96)	272·5 (4·17)	298 (3.45)	•
7-Cl	228(4.55)	258sh (3.76)	262sh (3.98)	272 (4.08)	298sh (3·26)	
4-Br	232(4.54)	257sh (3·31)	264 (3·77)	273(4.04)	298sh (3·32)	
5-Br	233(4.60)	257 sh (3.51)	264sh (3.81)	272(4.02)	297 (3.56)	<b>304 (3·62)</b>
6-Br	228 (4.55)	257 (3.21)	264sh (3.92)	273 (4-19)	• •	304sh (3·45)
7-Br	230(4.55)	256sh (3·48)	265 (3.92)	272·5 (4·05)	298 (3·31)	
4-F	223 (4.55)			262(4.21)		
5-F	222(4.40)			267.5(4.22)	290sh (3·99)	297sh (3·91)
6-F	223 (4.53)			264 (4.21)	289sh (3·86)	
7-F	223 (4.51)			268.5 (4.24)		
<i>x</i> -Br-4-F	228 (4.55)		264sh (4·05)	$273 (4 \cdot 28)$	293sh (3·86)	

band most noticeably affected by substitution in the phenyl ring; the remaining bands at 3260-3280 and 3160-3180 cm.<sup>-1</sup> are thus related to the primary aminogroup.

of 2-Aminobenzothiazoles.—Benzothiazole Spectra shows four main absorption bands<sup>41</sup> which are bathochromically displaced in 2-aminobenzothiazole; the u.v. spectra of halogenated derivatives (Table 3) show the presence of several minor inflexions in addition to the three bands previously 41,42 reported. The main bands in the 230 and 270 mµ region are both bathochromically displaced by halogen substitution in the order  $Br \ge Cl > F > H$ , irrespective of the orientation of the halogen atom, in agreement with an earlier 43 observation for 6-substituted 2-aminobenzothiazoles.

Principal i.r. absorption bands in the NH stretching region are shown in Table 4; previously reported values for some related derivatives (in dilute CCl<sub>4</sub>) show <sup>44</sup> asym. NH stretching at 3480 cm.<sup>-1</sup> and sym. NH stretching at 3412 cm.<sup>-1</sup>; in more concentrated solution these are replaced by bands at 3280 cm.<sup>-1</sup> (association of

obtained from other studies.45-47 The bands in the 3270 cm.<sup>-1</sup> region are at a somewhat lower frequency

## TABLE 4 NH stretching frequencies of halogenated 2-aminobenzothiazoles

Subst. in Ph ring					
н	3395 48	3478 48		(in	CHCl <sub>2</sub> )
	3395		3270	•	0/
6-NO,		3460	3295		
4-Cl		3468	3275		
5-Cl	3390		3270		
6-C1		3460	3270		
7-Cl	3400	3460	3470		
4-Br		3455	3278		
5-Br	3390		3264		
6-Br		3454	3270		
7-Br		3460	3295		
4-F		3475	3280		
5-F	3390		3270		
6-F	3388		3268		
7-F	3393		3262		
2-Aminothiazole 48	3395	3478		3311	۱
2-Imino-3-methyl-					
thiazole 48	3335				in CHCl <sub>a</sub>
2-Imino-3-methyl-					
benzothiazole 48	3350				1

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they are relatable to association phenomena; the bands in the 3470 and 3400 cm.<sup>-1</sup> region are ascribed to asym. and sym. stretching vibrations respectively.

All the 2-aminobenzothiazoles diazotised readily in glacial acetic acid or 50% aqueous sulphuric acid with nitrosyl sulphuric acid, and thence, by coupling to N-substituted anilines, gave brilliant red dyes which coloured synthetic fibres in deep shades. The properties of these dyes will be reported later.

## EXPERIMENTAL

4-Halogeno-2-aminobenzothiazoles.--6-Chloro-6and (80.8%), m.p. 201-202° (ethanol) (lit., 198°; 7 202° 52), 6-bromo- (21.4%), m.p. 216-218° (ethanol) (lit., 211-212°; 24  $234^{\circ}$  <sup>53</sup>), and 6-fluoro-2-aminobenzothiazole (48.7%), m.p. 183-184° (20% aq. ethanol) (lit.,<sup>23,54</sup> 181-182°), were prepared by thiocyanation-cyclisation<sup>55,56</sup> of the 4-halogenoanilines. Alternatively, reaction of 4- or 2-halogenoanilines with ammoniun thiocyanate in monochlorobenzene<sup>27</sup> gave 4-chloro- (68%), m.p. 180-181° (9:1 ethanol-acetone) (lit., 174-175°; 57 183° 58), 4-bromo- (95.4%), m.p. 183-184° (4:1 ethanol-acetone) (lit.,<sup>57</sup> 183-184°), 4-fluoro- (75.2%), m.p. 159-160° (benzene) (lit.,23 164°), 2-chloro- (78.3%), m.p. 144-145° (benzene) (lit.,<sup>22</sup> 146°), 2-bromo- (69.8%), m.p. 125-126° (ethanol) (lit., 59 125°), and 2-fluorophenylthiourea (93.6%), m.p. 143-144° (10% aq. ethanol) (Found: C, 49.1; H, 4.2; N, 16.6; S, 18.6. C<sub>7</sub>H<sub>7</sub>FN<sub>2</sub>S requires C, 49.4; H,  $4\cdot1$ ; N,  $16\cdot5$ ; S,  $18\cdot8\%$ ). Cyclisation of these with bromine in chloroform 52 gave 6-chloro- (98%), 6-bromo-(90%), 6-fluoro- (98%), 4-chloro- (95·4%), m.p. 206-207° (ethanol) (lit., 27 202-203°), and 4-bromo-2-aminobenzothiazole (63.8%), m.p. 219-220° (ethanol) (Found: C, 36.8; H, 2.1; Br, 34.6; N, 12.3; S, 14.0. C<sub>7</sub>H<sub>5</sub>BrN<sub>2</sub>S requires C, 36.7; H, 2.2; Br, 34.9; N, 12.2; S, 14.0%). From 2-fluorophenylthiourea were obtained white needles (20% aq. ethanol) (49.8%), m.p.  $219-220^{\circ}$ , of x-(6?)bromo-4-fluoro-2-aminobenzothiazole (Found: C, 33.8; H, 1.8; N, 11.5; S, 13.0. C<sub>7</sub>H<sub>4</sub>BrFN<sub>2</sub>S requires C, 34.0; H, 1.6; N, 11.3; S, 12.95%). Presence of this, and of unbrominated material, in the crude reaction mixture was indicated by mass spectra; the above was the principal product isolated from cyclisation procedures above 12 hr., but on decreasing cyclisation time to 6-7 hr., the main product isolates was white needles, m.p.  $138-140^{\circ}$  (72.4%)

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(20% aq. ethanol), of 4-fluoro-2-aminobenzothiazole (Found: C, 49.8; H, 2.9; N, 16.7; S, 19.0. C<sub>7</sub>H<sub>5</sub>FN<sub>2</sub>S requires C, 50.0; H, 3.0; N, 16.5; S, 19.3%).

5-Halogeno-2-aminobenzothiazoles.-A suspension of the appropriate 4-halogeno-2-nitroaniline (0.1 mole) in conc. sulphuric acid (30 c.c.) and water (30 c.c.) was diazotised  $0-3^{\circ}$  for 90 min. with 20% aqueous sodium nitrite (37.5 c.c.); after addition of potassium thiocyanate (10 g.) in water (20 c.c.), the diazo-liquor was stirred vigorously into a suspension of cuprous thiocyanate (18 g.) in water (60 c.c.) at 5°; after stirring for 2 hr. at 5° and then heating at  $70^{\circ}$ for 20 min., the mass was cooled overnight, filtered, and the cake extracted with boiling benzene to give 2-thiocyanato-5-chloronitrobenzene (61.7%), straw-coloured needles, m.p. 115—116° (ethanol) (lit.,<sup>60</sup> 116.5°) [ $\nu$ (CN) 2165 cm.<sup>-1</sup>], 2-thiocyanato-5-bromonitrobenzene (86.4%), pale orangebrown needles, m.p. 128° (ethanol) (lit.,60 131°) [v(CN) 2163 cm.<sup>-1</sup>], and 2-thiocyanato-5-fluoronitrobenzene (69.2%), buff coloured needles, m.p. 84–85° (ethanol) [v(CN) 2160 cm.<sup>-1</sup>] (Found: C, 42.1; H, 1.6; N, 13.9; S, 16.0. C<sub>7</sub>H<sub>3</sub>FN<sub>2</sub>O<sub>2</sub>S requires C, 42.4; H, 1.4; N, 14.1; S, 16.2%).

Reduction-cyclisation of the above, using a tin-hydrochloric acid procedure, 61, 62 was effected by stirring the above 2-nitrothiocyanato-derivative (10 g.) into conc. hydrochloric acid (120 c.c.) and adding granulated tin (40 g.) during 1 hr. After stirring at room temperature for 8 hr. and boiling a further 3 hr., the liquor was diluted with water, ammonia added, and the resultant white residue filtered after standing overnight and extracted with benzene to give 5-chloro- (78.9%), m.p. 202-203° (benzene) (lit.,<sup>28</sup> 198°), 5-bromo- (44.7%), m.p. 196-198° (ethanol) (Found: Br, 35.2; N, 12.4; S, 13.9. C7H5BrN2S requires Br, 34.9; N, 12.2; S, 14.0%), and 5-fluoro-2-aminobenzothiazole (84.9%), m.p. 199-200° (ethanol) (Found: C, 49.8; H, 2.9; N, 16.8; S, 19.1. C<sub>7</sub>H<sub>5</sub>FN<sub>2</sub>S requires C, 50.0; H, 3.0; N, 16.7; S, 19.0%). Alternatively, a mixture of 2-nitrothiocyanato-derivative (10 g.), ethanol (30 c.c.), water (25 c.c.), and conc. hydrochloric acid (25 c.c.) was refluxed gently during the addition of hydrogenreduced iron powder (20 g.). After refluxing for 16 hr., the liquor was filtered hot, cooled, the residue filtered, dissolved in hot water (Norit), and neutralised with ammonia to give 5-chloro-2-aminobenzothiazole (88.2%). Similar procedures, with suitable adjustment of solvent ratios to enable the amine hydrochloride to be filtered in good yield from the cooled liquor, gave 5-bromc- (77.8%) and 5-fluoro-2-aminobenzothiazole (89.6%).

5-Chloro-2-aminobenzothiazole was also obtained by cyclisation of 3-chlorophenylthiourea<sup>57</sup> (10 g.); fractional crystallisation from ethanol gave straw coloured plates (4.4 g.) of 5-chloro-2-aminobenzothiazole. The motherliquors gave white needles (3.68 g.), m.p. 144-151°, which yielded 1.87 g. of 7-chloro-2-aminobenzothiazole, m.p. 169-170° (ethanol) (lit., 28 145-150°).

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 &</sup>lt;sup>50</sup> D. Garfinkel and J. T. Edsall, J. Amer. Chem. Soc., 1958, 80, 3807. <sup>51</sup> C. N. R. Rao and R. Venkatavaghavan, *Canad. J. Chem.*,

g.) was chlorinated  $^{63}$  with t-butyl hypochlorite (50 g.) to give a deep orange material (69.8 g.), which was separated by column chromatography on alumina using benzene as solvent and eluent. A lower of two brown-orange zones was eluted to give intense orange prisms (29.7 g.) of 6-chloro-2-nitroaniline, m.p.  $76^{\circ}$  (the upper zone contained the 4-chloro-isomer).

6-Chloro-2-nitroaniline was also obtained by nitrating a solution of o-chloroacetanilide (22.2 g.) in glacial acetic acid (12 c.c.) and acetic anhydride (16 c.c.) at  $-5^{\circ}$  with nitric acid  $(d \ 1.54)$  (10 c.c.) in acetic acid (10 c.c.). After stirring at  $-5^{\circ}$  for 2 hr., the liquor was allowed to stand at room temperature for 48 hr., added to ice-water (350 c.c.), and filtered. The cake was washed neutral and slurried into ice-cold Witt-Utterman solution<sup>31</sup> (75 g. of potassium hydroxide in 475 c.c. of water and 100 c.c. of absolute ethanol) (90 c.c.) for 3 min., filtered rapidly, and the insoluble residue washed with ice-cold Witt-Utterman solution  $(2 \times 30$  c.c.) and then with cold water. The residue, straw coloured (8.4 g.) was essentially pure 4-nitro-2-chloroacetanilide, m.p. 139-141°. The filtrate, acidified with acetic acid, gave a yellow deposit of 6-nitro-2-chloroacetanilide (9.7 g.), m.p. 199-201°, hydrolysed by boiling for 30 min. in 50% aqueous hydrochloric acid to 6-chloro-2-nitroaniline (overall yield, 28.9%), m.p. 74-75°.

6-Bromo-2-nitroaniline, m.p.  $73-74^{\circ}$ , and 6-fluoro-2-nitroaniline, m.p.  $73^{\circ}$ , were prepared by nitration of 2-bromoacetanilide <sup>32, 64</sup> and 2-fluoroacetanilide, <sup>65</sup> and separation of the nitration mixture with Witt-Utterman solution.

The 6-halogeno-2-nitroanilines (0.05 mole) were diazotised in 50% sulphuric acid (50 c.c.) (or in a mixture of glacial acetic acid and conc. sulphuric acid) at  $0-5^{\circ}$  for 2 hr. with

<sup>63</sup> K. H. Pausacker and J. G. Scroggie, Austral. J. Chem., 1959, 12, 430.

nitrosylsulphuric acid prepared from sodium nitrite (3.5 g.) and conc. sulphuric acid (15 c.c.). A slurry of potassium thiocyanate (6 g.) in water (15 c.c.) was added, and after stirring for 5 min., the liquor was added rapidly to a well stirred suspension of cuprous thiocyanate (15 g.) in water (30 c.c.). Isolation as above gave 2-thiocyanato-3-chloronitrobenzene (82.4%), m.p.  $63-64^{\circ}$  (20% aq. ethanol), [v(CN) 2168 cm.<sup>-1</sup>] (Found: Cl, 16.55; N, 13.0; S, 14.9.  $C_7H_3ClN_2O_2S$  requires N, 12.9; S, 15.2; Cl, 16.8%), 2-thiocyanato-3-bromonitrobenzene (81.6%), m.p. 56-58° (ethanol) [v(CN) at 2160 cm.<sup>-1</sup>] (Found: Br, 30.5; N, 10.6; S, 12.2. C<sub>7</sub>H<sub>3</sub>BrN<sub>2</sub>O<sub>2</sub>S requires Br, 30.9; N, 10.8; S, 12.35%), and 2-thiocyanato-3-fluoronitrobenzene (75.3%), m.p. 59—60° (20% aq. ethanol)  $[v(CN) 2162 \text{ cm}.^{-1}]$  (Found : N, 13.9; S, 16.0. C<sub>7</sub>H<sub>3</sub>FN<sub>2</sub>O<sub>2</sub>S requires N, 14.1; S, 16.2%).

Reduction-cyclisation of the above with tin-hydrochloric acid (as above) gave 7-chloro-2-aminobenzothiazole  $(83 \cdot 5\%)$ , m.p. 169—170° (lit.,<sup>28</sup> 145—150°) (not depressed on admixture with the product obtained by cyclisation of 3-chlorophenylthiourea), 7-bromo-2-aminobenzothiazole (70%), m.p. 196—197° (ethanol) (Found: C, 36·4; H, 2·1; Br, 35·2; N, 12·6; S, 13·8. C<sub>7</sub>H<sub>5</sub>BrN<sub>2</sub>S requires C, 36·7; H, 2·2; Br, 34·9; N, 12·2; S, 14·0%), and 7-fluoro-2-aminobenzothiazole (58·3%), m.p. 210—211° (benzene or 30% aq. ethanol) (Found: C, 49·8; H, 2·7; N, 16·6; S, 18·7. C<sub>7</sub>H<sub>5</sub>N<sub>2</sub>SF requires C, 50·0; H, 3·0; N, 16·7; S, 19·0%). The latter was also prepared in 69·5% yield using hydrogen-reduced iron and hydrochloric acid.

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<sup>64</sup> H. Franzen and E. Engel, J. prakt. Chem., 1921, (2) 102, 156.
<sup>65</sup> B. M. Wepster and P. E. Verkade, Rec. Trav. chim., 1949, 20 - ---